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Synthesis and Characterization of Complexes of *vic*-Dioxime Derivatives with Transition Metal

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A novel *vic*-dioxime compound (H_2L) and their transition metal complexes were synthesized for the first time. This compound, N-[(4-(2,4-dihyroxybenzylideneamino)naphthalen-1-yl)]-N'-hydroxy-2-(hydroxyimino)acetimidamide, have been synthesized by starting metarial of naphthalene. The complexes of nickel(II), copper(II) and cobalt(II) with H_2L were prepared. The ligand and its metal complexes were charecterized FT-IR, UV, ^1H NMR, ^{13}C NMR, MS, elemental analysis and conductometric measurements.

Key Words: Metal complexes, Conductometric measurements, *vic*-Dioximes, Iminoximes and Characterization.

INTRODUCTION

The coordination chemistry of *vic*-dioximes is an intensive area of study and numerous transition metal complexes of these ligands have been investigated[1-5]. The presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make *vicinal* dioximes amphoteric ligands which form corrin-type, square-planar, square-pyramidal or octahedral complexes with transition metal ion such as copper(II), nickel(II) and cobalt(II) as central atoms[5-7]. Morever, investigated fields for these compounds concern liquid crystal, gas sensors and inhibitors for chemical warfare agents[8-11].

In this study, we prepared amphi-chloroglyoxime, anti-choloroglyoxime, 4-nitro-1-naphthylamine and FeO(OH) according to litareture[12,13]. A novel *vic*-dioxime, N-[(4-(2,4-dihyroxybenzylideneamino)-naphthalen-1-yl)]-N'-hydroxy-2-(hydroxyimino)acetimidamide (H_2L), have been synthesized by starting metarial of naphthalene and its Ni(II), Co(II), Cu(II) complexes were prepared[5].

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EXPERIMENTAL

$C_2H_3O_2Cl_3$, Na_2CO_3, $NH_2OH{\cdot}HCl$, KOH, $N_2H_4{\cdot}H_2O$, $NaHCO_3$, C_2H_5OH, NaOH, $Ni(CH_3COO)_2$, $Cu(CH_3COO)_2$, $Co(CH_3COO)_2$, were obtained from Merck (KGaA, Germany) and all of them were purified according to literature[14].

The carbon, hydrogen and nitrogen analyses were obtained using a Carlo Erba 1106 autoelemental analyzer. Jasco FT/IR-300 E spectrometer was used for characterization. The elektronic spectra in the 200-800 nm range were recorded in DMF on a Shimadzu UV-160 A spectrophotometer. Conductivities were measured in DMF using a LF330/SET conductivity meter and were performed at 24 ºC. Magnetic moments were measured by the Gouy method by using $Hg[Co(SCN)_4]$ as calibrant. ^1H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance-500 NMR instrument.

Synthesis of 4-[(4-nitronaphthalen-1-ylimino)methyl]benzene-1,3-diol (Sch)[2]: 4-Nitro-1-naphthylamine (5.64 g, 0.03 mol) dissolved in absolute ethanol (150 mL), was added with constant stirring to a solution 2,4-hydroxybenzaldehyde (4.14 g, 0.03 mol) in 30 mL absolute ethanol. The mixture was allowed to stir magnetically and refluxed for 36 h. After cooling, resulting precipitate was filtered, recrystallized by absolute ethanol, washed several times with hexane and dried over calcium chloride under vacuum. Yield: 46 % , m.p. 176 °C. Mass spectra: m/e 308.

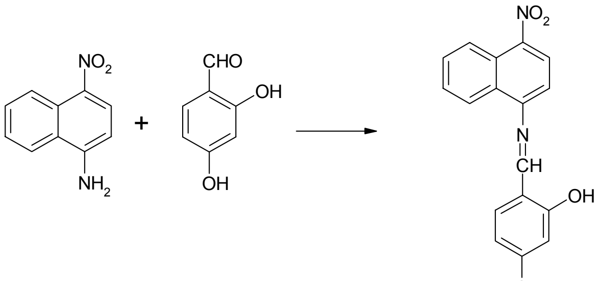

Fig. 1.

Synthesis of 4-[(4-aminonaphthalen-1-ylimino)methyl]benzene-1,3-diol (L): 0.42 g FeO(OH) as catalyst was first activated in water for 0.5 h and was added to the solution of Sch (4.20 g, 0.014 mol in 130 mL absoulte ethanol). In this mixture, solution hydrazinium hydroxyde ($N_2H_4{\cdot}H_2O$, 1.00 g in 20 mL absoulte ethanol) was added dropwise for 5 min and refluxed for 5 h. Catalyst was filtered off after cooling the content of the flask to room temprature. Excess ethanol was removed under vacuum to give yellow solid. The product recrystallized by absolute ethanol, washed several times with cold hexane and dried over calcium chloride under vacuum[15]. Yield: 88 %, m.p. 112 ºC. Mass spectra: m/e 278.

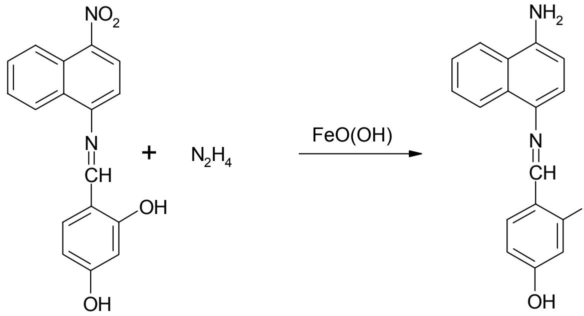

Fig. 2.

Synthesis of N-[4-(2,4-dihydroxybenzylidenamino)naphthalene-1-yl]-N'- hydroxy-2-(hydroxyimino)acetimidamide (H_2L): A water solution of $NaHCO_3$ (0.67 g, 8 mmol) was added to a solution of L (1.12 g, 4 mmol in 10 mL absolute ethanol), then a solution of *anti*-chloroglyoxime (0.49 g, 4 mmol in 10 mL absolute ethanol) which is synthesized by the method described previously was added dropwise to the mixture at room temperature over 2 h. The mixture was stirred on a water bath at 60-70 ºC for 5 h more[16]. The mixture was filtered and excess of ethanol was removed by evaporation through a rotary evaporator. The product was precipitated by the addition of ethanol. Obtained product was filtered off and dried in vacuum. Yield: 69 %, m.p. 152 ºC. In the MS spectra of the H_2L ligand, m/e 364. ^{13}C NMR ($CDCl_3$): δ (ppm) 163.8, 163.1, 159.9, 157.6, 149.7, 142.8, 140.1, 130.4, 129.0, 128.0, 126.4, 125.2, 122.2, 121.4, 119.6, 118.0, 115.0, 109.0, 103.8.

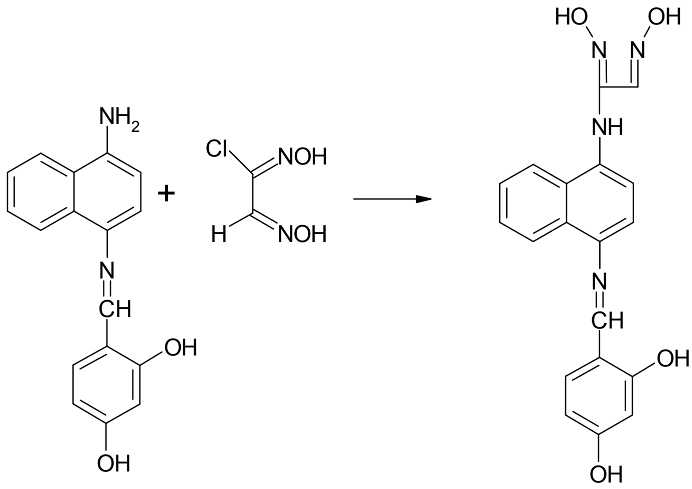

Fig. 3.

Synthesis of the $Ni_3(H_2L)_2{\cdot}4H_2O$ complexes: A solution of 0.21 mmol metal salt [$Ni(CH_3COO)_2{\cdot}6H_2O$, 0.051 g] in 10 mL distilled water were added to the 0.041 mmol solution of the ligand (H_2L 0.15 g) in 15 mL ethanol. The pH of the mixture was adjusted to 6.0-6.5 with the addition of 1 % NaOH solution. In order to complete the precipitation, the mixture was refluxed for 3 h before filtration. The complex formed was filtered off, washed with cold water and hexane, then dried in vacuum. Yield: 51 %, m.p. 260 ºC (decomposition point). The structure of the complex is given in Fig. 4.

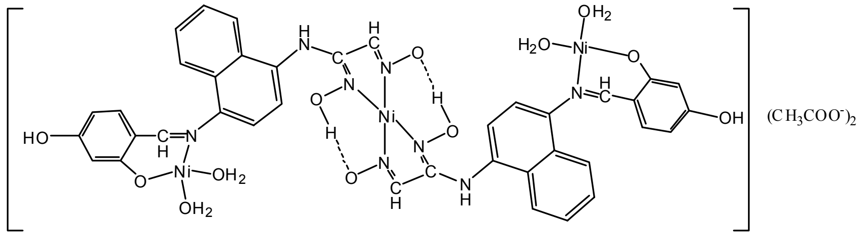

Fig.4.

Synthesis of the $Co_3(H_2L)_2{\cdot}10H_2O$ complexes: A solution of 0.205 mmol metal salt [$Co(CH_3COO)_2{\cdot}4H_2O$, 0.051 g] in 10 mL distilled water were added to the 0.041 mmol solution of the ligand (H_2L 0.15 g) in 15 mL ethanol. The pH of the mixture was adjusted to 6.0-6.5 with the addition of 1 % NaOH solution. In order to complete the precipitation, the mixture was refluxed for 3 h before filtration. The complex formed was filtered off, washed with cold water and hexane, then dried in vacuum. Yield. 80 %, m.p. > 300 ºC. The structure of the complex is given in Fig. 5.

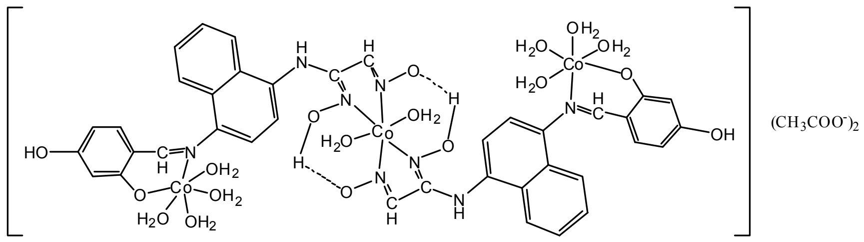

Fig. 5.

Synthesis of the $Cu(H_2L)_2$ complexes: A solution of 0.205 mmol metal salt [$Cu(CH_3COO)_2·H_2O$, 0.041 g] in 10 mL distilled water were added to the 0.041 mmol solution of the ligand (H_2L 0.15 g) in 15 mL ethanol. The pH of the mixture was adjusted to 6.0-6.5 with the addition of 1 % NaOH solution. In order to complete the precipitation, the mixture was refluxed for 3 h before filtration. The complex formed was filtered off, washed with cold water and hexane, then dried in vacuum. Yield: 49 %, m.p. > 300 ºC. The structure of the complex is given in Fig. 6.

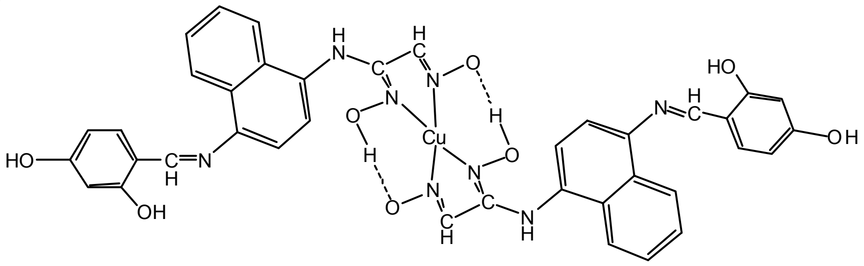

Fig. 6.

RESULTS AND DISCUSSION

The analytical data for the ligands and their metal complexes are listed in Table-4. The composition of the complexes are [$M_3(H_2L)_2$] for Ni and Co and $M(H_2L)_2$ for Cu. The schiff base ligand (H_2L) is soluble in common organic solvents. All complexes are soluble in DMF , DMSO and insoluble in the other organic solvents.

The tentative assigment of the most charecteristic IR bands were observed and are given in Table-3. The vibration of the sterically hindered of oxime groups of the free schiff base ligand oxime [H_2L] were observed 3400-3500 cm^{-1}, respectively[17,18]. When the spectra of the complexes compared with those of the uncomplexed schiff base, the ν(C=N) band are shifted to lower frequency[19-21]. This indicates that the imine nitrogen is coordinated to the metal ion. The spectra of complexes show a few expected absorbtion bands 550-558 and 420-440 cm^{-1} ranges assigned to ν(M-N)[19,22] and ν(M-O)[20], respectively.

The electronic absorption of the ligand and its metal complexes are given in Table-1. In the spectra of the schiff base ligand bands at 211-267 nm are attributed to the benzene π-π* transtions[23-25]. The bands at 321-431 nm are assigned to the imine π-π* transition. In comparison to the free ligand, the imine π-π* transitions of the complexes were shifted to some extent, because the imine nitrogen is involved in coordination with the metal ion.

TABLE-1
MAGNETIC MOMENTS AND ELECTRONIC SPECTRAL DATA OF THE SCHIFF BASE LIGAND AND THEIR METAL COMPLEXES

Compound	μ_{eff} (BM)	λ_{max} (nm)
H_2L	–	402; 317; 244(s); 210
$Ni_3[H_2L]_2.4H_2O$	Diamag.	430; 399(s); 322; 265; 251; 229
$Co_3[H_2L]_2.10H_2O$	3.66*	566(s); 523; 476; 233
$Cu[H_2L]_2$	1.70	451; 441(s); 429(s); 400; 333; 323; 298

*For each Co atom; (s): shoulder

TABLE-2
^{1}H NMR SPECTRA OF THE SCHIFF BASE LIGANDS

Compd.	δ (ppm)	Assignment
Sch	9.2 (s, 1H)	Ph-CH=N-
	8.6(d,1H)-8.2(d,1H)-8.1(d,1H)-8.0(d,1H)-7.8(d,1H)-7.5(d*d,1H)-7.4(d*d,1H)-7.3(t,1H)-7.2(t,1 H)	Aromatic ring (H)
	15.4 (s, 2H)	Phenolic OH
L	9.2 (s, 1H)	Ph-CH=N-
	8.6(d,1H)-8.2(d,1H)-8.1(d,1H)-8.0(d,1H)-7.8(d,1H)-7.5(d*d,1H)-7.4(d*d,1H)-7.3(t,1H)-7.2(t,1 H)	Aromatic ring (H)
	15.4 (s, 2H)	Phenolic OH
	3.3 (s, 2H)	NH_2
H_2L	12 (s, 2H)	=NOH
	9.2 (s, 1H)	Ph-CH=N-
	8.6(d,1H)-8.2(d,1H)-8.1(d,1H)-8.0(d,1H)-7.8(d,1H)-7.5(d*d,1H)-7.4(d*d,1H)-7.3(t,1H)-7.2(t,1 H)	Aromatic ring (H)
	6.4(s, 1H)	-CH=N-
	15.4 (s, 2H)	Phenolic OH
	3.0 (s, 1H)	NH

The molar conductance values of the synthesized schiff base ligand and its Ni(II), Co(II) and Cu(II) complexes are in the range 10 to 35 Ω^{-1} cm^2 mol^{-1} in 10^{-3} M DMF solutions indicating the non-electrolytic nature of these compounds[23].

In order to understand the solution structure of the a novel oxime and free schiff base ligands, ^{1}H NMR spectra have been employed. ^{1}H NMR assignments were listed in Table-2. The singlet (2H) observed at 12 and 15.4 ppm were assigned =NOH and phenolic -OH proton of ligand H_2L. The singlet (1H) observed at 9.2 and 6.4 ppm were assigned to the

TABLE-3
INFRARED SPECTRAL DATA OF THE LIGANDS AND ITS COMPLEXES

Compound	ν(O-H)	ν(C=N) imine	ν(C=N) oxime	ν(N-H)	ν(C-H) aromatic	ν(C=C)	ν(C-N)	ν(N-O)	ν(M-N)	ν(M-O)
Sch	3500	1640	-	-	3070-3030	1450-1600	1154	985	-	-
L	3500	1640	-	3200-3300	3070-3030	1450-1600	1150	-	-	-
H_2L	3400-3500	1640	1625	3300	3070-3060	1450-1600	1150	970	-	-
$Ni_3[H_2L]_2.4H_2O$	3300 (H_2O)	1640	1625	-	3070-3060	1450-1600	1165	950	525	400
$Co_3[H_2L]_2.10H_2O$	3300 (H_2O)	1640	1625	-	3070-3060	1450-1600	1165	960	560	410
$Cu[H_2L]_2$	3500	1640	1625	3290	3070-3060	1450-1600	1150	960	550	420

TABLE-4
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF THE SCHIFF BASE LIGANDS AND METAL COMPLEXES

Compound	m.f.	m.w.	Colour	m.p. (ºC)	Yield (%)	Found (Calcd.) %		
						C	H	N
Sch	$C_{17}H_{12}N_2O_4$	308.3	Orange	176	46	66.19 (66.23)	3.88 (3.92)	8.83 (9.09)
L	$C_{17}H_{14}N_2O_2$	278.3	Black	112	88	73.02 (73.37)	4.91 (5.07)	9.56 (10.07)
H_2L	$C_{19}H_{16}N_4O_4$	364.4	Brown	152	69	62.50 (62.63)	4.34 (4.43)	15.01 (15.38)
$Ni_3[H_2L]_2.4H_2O$	$C_{42}H_{42}N_8O_{16}Ni_3$	1090.9	Dark Brown	260*	51	46.19 (46.24)	3.53 (3.88)	9.83 (10.27)
$Co_3[H_2L]_2.10H_2O$	$C_{42}H_{54}N_8O_{22}Co_3$	1199.7	Brown	>300	80	41.48 (42.05)	4.18 (4.54)	9.07 (9.34)
$Cu[H_2L]_2$	$C_{38}H_{30}N_8O_8Cu$	790.2	Red	195	49	56.90 (57.76)	3.75 (3.83)	14.01 (14.18)

*Decomposition points of corresponding molecule.

protons of Ph-CH=N-Napht and -CH=N- the proton of the group, respectively. The multiplex (9H) observed at 8.6-7.2 ppm were assigned to the aromatic ring proton of the ligand H_2L. Furthermore the singlet at 15.4 and 3.0 ppm in the ligand H_2L were attributed to the protons of phenolic -OH and -NH group.

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